Chemical Structure of Bituminous Coal

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Introduction

The purpose of this paper is to survey present knowledge of the structure of coals in such a way as to provide a useful background to consideration of the production of chemical by-products. In addition some deductions will be drawn from structural knowledge about the probable contribution made by different coal components and by different parts of the structure to the volatile matter evolved on carbonization. Since the survey has only this limited objective, no attempt will be made to treat the subject exhaustively; and since detailed, fully documented, reviews have appeared recently[1,2], a full bibliography is not provided.

Examination of a sample of coal with the naked eye or under the microscope reveals that the material is apparently heterogeneous. There are bands of different reflectance running through the coal, and even minute areas scanned microscopically show a variation of optical properties; moreover, there are regions showing various types of fossilized plant remains. These components have been classified in various ways, and there is no universally agreed system; moreover, the subject is complex since a large number of alleged components have been distinguished. The term "alleged" is used in recognition of the fact that the significance of a component can only be established to the satisfaction of coal scientists at large if it has been separated physically and shown to differ appreciably in chemical and physical properties and in carbonization behavior from material associated with it in the whole coal. The real significance of many components has not yet been established in this way.

For present purposes it will be sufficient to postulate that bituminous coals are composed of three major "maceral" groups, which, in the common European terminology are known as vitrinite, exinite and inertinite. The term "inertinite" refers to components inert in carbonization; "inert" does not imply that the materials undergo no chemical reaction, only that they do not soften or swell on heating and contribute little to the volatile matter. Vitrinite is quantitatively the most important maceral, accounting for probably 60-80% of most worked coals, and it is the material primarily responsible for the characteristic coking behavior of higher rank bituminous coals. Coals relatively rich in the other components are known, but they are rare in the U.S.A.; nevertheless, even in minor amount, they can make significant contributions to the properties of the whole coal.

In what follows, the structure of vitrinites will be considered first. So far as possible the conclusions stated will be based on work with pure macerals, but some evidence relative to vitrains (bright bands of coal seams, normally containing 80-95% vitrinite) will be used where it seems improbable that the character of broad qualitative conclusions could be altered by the presence of small amounts of petrographic impurity. After the consideration of vitrinites, available evidence on structural differences between them and other macerals will be reviewed; at this point some comments will be made on the sub-components of the main maceral groups.

The Structure of Vitrinites

It has long been believed that vitrainous coals are predominantly aromatic in structure. The partly aromatic nature of coals is established qualitatively by the presence of certain bands in their infra-red spectra. However, the fullest

and most convincing evidence on this point comes from the study of the scattering of x-rays by coals. The interpretation of the scattering data is a difficult and complex business, and no completely adequate treatment has yet been devised. The method most recently published[3] makes use of a curve-fitting procedure, in which the scattering curve calculated for various hypothetical models is compared with the curve observed experimentally. Of the models tested, the one that gave the best fit required the supposition that in bituminous vitrinites a majority of the carbon was organized into aromatic nuclei containing on the average 2-3 fused rings. For reasons that need not be discussed here the published work does not permit any accurate estimate of the fraction of carbon atoms in such systems nor any information about the other carbon atoms. The indications from the x-ray work, and the study of infrared spectra, are that the aromaticity is between about 60 and 85%, increasing with rank, though lesser figures are possible. Further work may alter this estimate but is unlikely to change much the sizes of the nuclei quoted above.

In view of its obvious importance, much ingenuity has been expended in trying to devise methods of calculating the aromaticity from such physical properties as density and refractive index by "physical constitution analysis". For what they are worth, the results are in accord with the figures just given.

Non-aromatic carbon must be presumed aliphatic, and indeed the infra-red spectra of vitrinites demonstate that aliphatic material is present. J. K. Brown[4] was able to estimate the ratio of aromatic to aliphatic hydrogen in a series of vitrains from the spectra, and his values have recently been confirmed (with a small revision towards higher values) by nuclear magnetic resonance studies[5,6]. It appears that vitrains of carbon content between 80 and 90% have the ratio H_{ar}/H_{al} rising from about 0.20 to 0.50, that is between 80 and 50% of the hydrogen is attached to aliphatic carbon atoms. The proportion of hydrogen in methyl groups cannot be measured by infra-red methods, but the relative intensity of the methyl vibration at 1375 cm.$^{-1}$[6] indicates that these groups are rare compared with CH_2. N.m.r. data confirm this[6], and indicate a fair proportion of tertiary $\rightarrow CH$. The spectra show that in the lower rank coals, the aromatic nuclei are highly substituted.

Many workers have studied phenolic hydroxyl in coals, by a variety of methods (see refs. 1, 2 for a review). It is established that between 40 and 80% of the oxygen in bituminous vitrinites is present at this type of functional group.[7] Most of the balance of the oxygen is in some form of strongly conjugated carbonyl[7].

Several groups of workers have investigated the dehydrogenation of hydroaromatic structures in coals, and it is now certain that much of the aliphatic hydrogen is attached to such structures rather than to alkyl groups or other forms of alicyclic rings[9,10]. The proportion of hydrogen removeable by two different dehydrogenation reactions falls from about 30-40% at a carbon content of 82-84% to 12-25% at 89-90% C. These figures correspond to <u>minimum</u> fractions of carbon in hydroaromatic rings in the region of 30 and 12% respectively. These data, together with n.m.r. and infra-red spectroscopic results, indicate that in the average composition of the aliphatic part of coals, CH_n, n is considerably less than 2, at least for the lower rank materials. This implies, though does not prove, that very little hydrogen or carbon can be present in alkyl groups or non-hydroaromatic alicyclic rings (it should be recalled that there is no evidence of the presence of olefinic or acetylenic groups in coals, which could also lead to a low value of n).

The molecular weights of coals are not known; determinations with solvent extracts[2] give values between about 500 and 3000. Therefore each molecule must contain a number of aromatic nuclei, linked together by non-aromatic groups. Attempts to make a synthesis of all the above information[2,10] show that it is difficult or impossible to suggest any type of molecular structure that does not employ the hydro-aromatic carbon as a means of linking the aromatic nuclei. The most obvious expression of this principle is the 1,2- and 1,4-cyclohexadiene ring present in the 9,10-dihydro-

phenanthrene and -anthracene molecules respectively, where two benzene rings are linked by two methylene groups which complete a third, non-aromatic, ring. Other possibilities have been discussed[2]. The "depolymerization" experiments of Heredy and Neuworth[11] also strongly suggest that the aromatic nuclei are linked together by methylene bridges, though here there is no necessary implication that these constitute hydroaromatic rings.

We have therefore arrived at the following picture of the structure of bituminous vitrinites. Each molecule contains a number of aromatic nuclei containing from 1 to 5 or 6 fused rings, the majority containing 1, 2 or 3 rings. Each aromatic nucleus contains few replaceable hydrogen atoms. The substituents are partly phenolic hydroxyl and carbonyl oxygen, and partly aliphatic carbon atoms that are disposed in such a way as to constitute hydroaromatic rings and to serve as linkages connecting the aromatic nuclei together. In addition there is a minor proportion of short alkyl chains and perhaps non-hydroaromatic alicyclic rings (the latter includes the cyclopentadiene ring system as found in indene and fluorene). Such molecules would be very markedly non-planar. As an illustration of what is meant by this description, Fig. 1 shows a segment of a hypothetical coal molecule.

It should be noted that on this view each coal molecule is a true statistical sample of the bulk material, in the sense that each contains all the known structural features in approximately the same proportions. The older view of coal structure as a kind of strawberry jam, containing lumps of graphitic material embedded in a continuous medium, the bitumen, therefore becomes meaningless. Furthermore, in the model proposed the aliphatic and aromatic parts are so intimately integrated in the molecular units that one cannot label one part as tar-forming and another as coke-forming.

Structure of Exinite and Inertinite Materials

The exinite or leiptinite suite includes a group of components not derived, like vitrinite and fusinite, from woody tissue. The most abundant member of the group, about which most is known, is sporinite, the remains of plant spores (indeed, the name exinite is often used to mean only this type of material). Sporinite contains considerably more hydrogen, and less oxygen, than the associated vitrinite. It is less soluble in organic solvents, more resistant to oxidation, and has a lower aromaticity (see the excellent review by J. K. Brown[12] and references therein). A group of spore exinites from British coal seams was found to contain more hydroaromatic hydrogen (corresponding to a minimum fraction of hydroaromatic carbon equal to about 0.4) than the associated vitrinites; less phenolic hydroxyl was found, both as a fraction of the weight of coal and as a fraction of the total oxygen[13]. The aromatic nuclei are about the same size as those in vitrinites, but the mean interlayer spacing is larger, suggesting that frequent occurrence of naphthenic structures keeps the planes apart[12]. It was concluded[13] that sporinites probably contain the same type of molecular structure as vitrinites, but that the molecules are larger, less polar and more hydroaromatic.

Exinites have a highly characteristic behavior on heating. Of whatever rank, they soften at around 400° and acquire a fluidity much too high to be measured with a Giessler plastometer. Even 60% exinite concentrates have fluidities greater than 20,000 divs per minute[14]. They swell enormously to a thin fragile bubble structure, which is so weak that a dilatometer piston sinks and resolidification cannot be observed this way. The loss in weight in the volatile matter test is much greater for exinites than for vitrinites and is in many cases 70-80%.

Little is known of the other members of the leiptinite suite. Resinite, the remains of plant resins and waxes, is widely distributed in samll amount, and also appears to be hydrogen-rich and very fluid when heated. The other components, cutinite (from cuticles), alginite (found only in boghead coals) and sclerotinite (from fungal sclerotia) are probably of little importance for present purposes.

The inertinite group contains two major components, fusinite and micrinite.

Fusinite closely resembles charcoal; its carbon content is always over 91%, it does not show fluidity or swelling, it contributes little to the volatile matter[12], and chemically it is relatively unreactive[15]. Micrinites have appreciably higher carbon and lower hydrogen contents than the associated vitrinites, though the difference is not so extreme as it is with fusinites. The aromatic nuclei are larger than in vitrinites. Both micrinites and fusinites are virtually opaque to infra-red radiation, and so no spectra have been reported. Both macerals undergo substitution with N bromosuccinimide, a reagent specific for placing bromine on aliphatic carbon in the α-position to a double bond (e.g. the methyl groups in propylene or toluene); this suggests that at least some aliphatic material is present[15,16] (see Table I). Both also contain some phenolic hydroxyl. Micrinites do not swell or become fluid on heating.

For convenient reference some properties of sets of macerals each separated from one seam are collected in Table I. Two German and four British coals are included; no corresponding data have yet been published for American coals so far as the author is aware. Data will be found in the Table that support the statements made above about differences in elemental composition, hydroxyl contents, etc. It will be noticed that the exinites associated with British and German vitrinites of closely similar rank differ considerably in yield of volatile matter.

Unfortunately reflectance data are not available for the samples quoted, and so some refractive indices are included as an indication of optical properties.

Chemical Changes on Heating
Little direct experimental evidence is available on this subject, but available information can be usefully supplemented by the results of experiments on models and by predictions from the type of structure believed to be present.

The phenolic hydroxyl content of bituminous vitrains drops sharply to low values when the coal is heated to 450-500°[18]. Preliminary experiments on two vitrains, using Peover's method with benzoquinone, suggest that the hydroaromatic hydrogen content also drops sharply in a similar or somewhat lower temperature range[18]. The infra-red spectra of vitrains heated to 400° shows little change, except that the aliphatic C-H and phenolic OH absorption are slightly weaker[19]. By 460° aliphatic CH is much weaker, and OH slightly so; the H_{ar}/H_{al} ratios of two vitrains of carbon contents 82 and 89% had reached 2.4 (values for the unheated coals were about 0.25 and 0.6 respectively, and for the higher rank coal heated to 400°, 0.8). By 550° both OH and aliphatic C-H are very weak, but the aromatic C-H bending frequencies at 700-900 $cm.^{-1}$ are still well-defined. Above this temperature the coals become opaque, owing no doubt to incipient graphitization. No significant changes in x-ray scattering are observed until a vitrain has been heated to 500°, at which temperature the growth of the aromatic nuclei begins to be noticeable[20]. Between 500 and 1000° there is further continuous growth, the average layer diameter of one sample, for example, increasing from 7A° to 14A°. It will be recalled that the free radical content of vitrain chars[21] passes through a sharp maximum at 500-550°, the maximum rate of volatile evolution occurs at about 450°, and electrical conductivity increases sharply (by many orders of magnitude) in the range 600-650°[22].

Dryden and his co-workers have studied the primary products of the evolution of volatile matter from vitrains by two methods: (a) study of the chloroform-soluble material extractable from coals heated very rapidly to temperatures near 400°; (b) distillation or pyrolysis of coals spread in thin layers on a heated plate in a high vacuum, a condenser being placed just above the plate. They find the extract and distillate to have closely similar infra-red spectra, and to resemble the original coal spectroscopically much more closely than a tar. These materials appear to play an important part in producing fluidity and resolidification to a coke when a coking coal is carbonized. They conclude that the materials mostly exist as such in the raw coal and are only to a small extent products of decomposition. However,

Table I. Properties of Macerals separated from British and German Coals.

Colliery and Seam Source of data,ref.	Markham Main, Barnsley 13, 14, 15			Dinnington Main, Barnsley 13, 14, 15			Zollverein 12, 17			Aldwarke Main, Silkstone 13, 14, 15				Chislet, No. 5 13, 14, 15			Anna 12, 17		
	V	E	F	V	E	F	V	E	M	V	E	F	M	V	E	F	V	E	M
%C, d.a.f.	82.3	81.6	91.6	85.1	84.3	92.4	85.7	87.4	88.0	86.9	87.1	92.1	87.1	88.6	89.1	92.2	88.4	89.1	89.6
H	5.5	7.6	3.6	5.3	7.6	3.1	4.9	6.7	4.2	5.4	7.4	3.7	4.6	5.3	6.2	3.8	5.1	5.0	4.3
O	9.3	8.4	3.4	6.9	5.7	3.5	7.8	4.7	6.8	4.9	4.2	3.0	6.0	3.9	3.6	2.7	4.7	3.8	5.0
%O as OH	5.7	3.7	0.8	5.1	2.9	-				3.9	1.4	0.5	2.2	2.8	0.8	0.4			
O$_{OH}$/O$_{total}$,%	61	45	13	74	52	-	32	59	23	80	31	12	35	72	20	10	28	37	19
V.M.	40.5	82	14	34.7	71	15				33	70	15	-	30.6	41	15			
Density (He)							1.30	1.19	1.39								1.30	1.27	1.39
Refr. index (5460A°)							1.84	1.67	1.95								1.90	1.82	2.01
Atoms Br added/100C (N.Br-succinimide)	13			13						14	17	2.0	8.5						

Note: V = vitrinite, E = exinite, F = fusinite, M = micrinite.

they are thermally unstable, and in carbonization at a more normal rate of heating they would undoubtedly decompose _in situ_ to a considerable extent.

The temperature of maximum rate of volatile evolution is about the same for exinites and micrinites as for vitrinites[12,17]. Ladam and Alpern carbonized a vitrinite concentrate and an exinite concentrate from the same coal seam at 600° and made a detailed analysis of the volatile products by vapor-phase chromatography. They found the products from the exinite concentrate to contain much more aliphatic material, more benzene homologues, more side-chain-substituted aromatics and less phenols. This result is in accord with the differences in structure believed to exist between the starting materials, and implies that the process of thermal decomposition does not, at least in their conditions, blur the effects of differences in structure.

It is well-known that the C-O bond in phenols is considerably weaker than the C-C, and that the C-H bond in the aliphatic parts of hydroaromatics is weaker than aromatic C-H. It is therefore reasonable to suppose that when molecules of the type attributed to vitrinites are heated, the primary changes will be homolytic dissociation of OH groups and loss of hydrogen from naphthenic rings, the latter resulting in thermal aromatization. It is likely that in an assembly of large complex molecules of the type described, where the changes of configuration required by aromatization may be difficult, that some of the hydroaromatic bridges will split rather than dehydrogenate; this may be the means whereby the aromatic material found in tar is broken off the main structure. These various changes will produce in the first instance OH radicals and H atoms, and leave free radical centres in the main structure, which would initiate further rearrangement and decomposition.

It is well known that little molecular hydrogen is evolved from coals until temperatures near 600° are reached. The hydrogen released by thermal dehydrogenation at lower temperatures must be consumed in saturating free readical centres in the volatile matter and the residue.

These ideas receive some confirmation from a series of experiments on the pyrolysis of model substances reported by van Krevelen and his co-workers[25]. These authors synthesized a number of polymers containing various substituted and unsubstituted aromatic nuclei linked and cross-linked by methylene bridges. They found that, on pyrolysis, unsubstituted hydrocarbon polymers showed a maximum rate of decomposition at about 500°, and split extensively at the bridge units, leaving little solid (coke) residue. On the other hand polymers containing naphthenic rings, or still more if they contained phenolic hydroxyl substituents, showed a maximum rate of decomposition at considerably lower temperatures and left a much greater amount of coke residue. They concluded that when substituents are present there is, competing with the normal depolymerization reaction, a direct condensation proceeding as a result of dissociation of the substituents, and the latter tends to produce molecular enlargement. In support of this suggestion of competing reactions they adduce the fact that when substituents are present the coke yield increases greatly with decreasing rate of heating.

There is one other factor that should be mentioned. The late D. H. Bangham pointed out[26] that volatile matter evolved inside a particle of coal may well have to diffuse in a mobile adsorbed film in fine pores to the outside; while so adsorbed it is exposed to surface forces that could promote secondary reactions and also could act as a lubricant in promoting fluidity. Since porosity varies with rank, passing through a minimum at a carbon content about 89%, the magnitude of these effects will also vary with rank.

There is no experimental evidence bearing on the chemistry of the pyrolysis of the inert macerals. From the nature of this structure one would deduce that some

stripping of peripheral groups would occur, permitting condensation with neighboring molecules, but little alteration of the basic skeletal structure. The behavior of inert macerals as seen with the hot stage microscope is beautifully demonstrated in the color film prepared by W. Spackman and his collaborators. Exinitic material can be seem to liquefy and flow round grains of inertinite, the morphology of the latter remaining almost unchanged.

A Chemical Description of Carbonization

A synthesis of the information given above permits a fairly detailed description of the main chemical phenomena of carbonization. The first major change is a softening of the "volatile solids", in Dryden's terminology, which, it is suggested, represent the lower molecular weight, hydrogen-rich, fraction of the coal. This softening is accompanied by the initiation of the decomposition of this fraction, and perhaps also of the involatile residue, the primary step being dissociation of hydrogen from hydro-aromatics, shortly followed by dissociation of OH. These chemical changes cause two principal secondary reactions, one leaving a more aromatic hydrogen-poor material and the other a breaking off of volatile partly aromatic fragments as a result of the de-stabilization of the main structure owing to radical formation in it. A limited amount of cross-linking may also occur, giving a more stable and less volatile residue. These various changes, initiated by dissociation of H and OH, are more or less complete by about 500-550°. By this stage, much of the oxygen has been stripped off and the aromatic nuclei have not grown much in size but the molecules are more highly cross-linked. Some of the free radical centres produced by decomposition remain as such, "trapped" in the carbon matrix.

At 600-650° enough energy is available to break a few aromatic carbon-carbon bonds, so that the carbon skeleton can rearrange and condense to larger polycyclic nuclei of lower H/C ratio, and hydrogen gas is released. These changes also permit the pairing of the odd electrons in the free radical centres. The dramatic change in electrical conductivity no doubt results partly from the growth of the aromatic lamellae, partly from the elimination of insulating material between the lamellae, and partly from a greater degree of order in their stacking.

These changes no doubt continue at a diminished rate at higher temperatures still, and some of the oxygen, nitrogen and sulfur is stripped out.

This description probably has some application to sporinites also. But it has been suggested that there may be an additional factor here[13]. The greater interlayer spacing in exinites and the less polar nature of the molecules will cause the inter-molecular forces of adhesion to be weaker than they are in vitrinites. This may be an important cause of the greater fluidity of exinites and the facility with which volatile matter escapes. Moreover, it will change the balance between van Krevelen's competing reactions, that is, the direct breakdown and the condensation to larger units resulting from dissociation of H and OH. In any case the ratio of hydroaromatic hydrogen to hydroxyl is much greater in exinites than vitrinites.

Discussion and Conclusions

The relevance of the above information and speculation to the production of chemical by-products from coal will be discussed with reference to hydrogenation, carbonization, and other methods.

(a) Hydrogenation

It is possible by use of a carbon catalyst, an elevated temperature, and a high partial pressure of hydrogen, to cause hydrogenolysis of alkyl groups in alkyl aromatics without saturating the ring; for example:

$$R.CH_3 + H_2 \rightarrow R.H + CH_4.$$
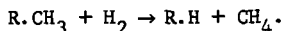
Ideally, this is in effect what one would wish to do in the hydrogenation of coal; the hydroaromatic parts of the structure would be eliminated as methane and ethane and the individual aromatic nuclei would be released as a mixture of relatively simple phenols, hydrocarbons and perhaps quinones or quinols. However, if the 1,2-cyclohexadiene type of linking unit, as in 9,10-dihydrophenanthrene, were common, stable single linkages between aromatic nuclei would remain in the product. Thus for example dihydrophenanthrene itself would give diphenyl and ethane, whereas the isomeric dihydroanthracene would give benzene and methane.

There are of course practical difficulties in contacting solid coal with a solid catalyst. For this reason, and because of the complexity of coal structure, such selectivity of hydrogenolysis is improbable. It is more likely that partial or complete saturation of the aromatic nuclei will precede any extensive hydrogenolysis of the linking units. Once saturation occurs, we are left with an extended naphthenic structure in which there is nothing to distinguish between the linking and aromatic parts of the original structure(except perhaps some oxygen substituents and heterocyclic atoms).

Perhaps, then, from a chemical point of view the best hope of breaking down coal structure to useful products by hydrogenation is to proceed in two steps, first a catalytic addition of hydrogen to the aromatic parts, and then a cracking, perhaps with a conventional cracking catalyst in a high-boiling oil.

The above remarks should apply equally to exinitic material. In carbonization one needs, in order to make a good coke, an optimum fluidity and not a maximum. In view of the difficulties of reactions involving two solid phases, in hydrogenation the maximum fluidity is clearly desirable, and so the greater the exinite content of the raw material the better. Indeed it would be desirable, if economically feasible, to use a blend of a coal with a black durainor other exinite concentrate.

On the other hand the inert components are two graphitic to be at all readily hydrogenated and broken down, and inasmuch as they will tend to decrease fluidity are undesirable contaminants of the raw material for hydrogenation.

(b)   Carbonization
Carbonization of coal is carried out in the U.S.A. almost entirely for the purpose of making coke, and it is doubtful how far the process can be modified merely to improve the yield or quality of by-products. However, since the purpose of this paper is to discuss the basic chemistry involved, this factor is ignored in what follows.
It seems likely that both the total yield of chemicals from coal carbonization and the content of useful materials will increase with the exinite content of the charge, even though in commercial operation the volatile matter is exposed to much secondary change. Since the yield of volatile matter from exinites is so much (50-100%) greater than that from vitrinites, the relatively small amount (10-25%) commonly found in whole coals charged to coke ovens can make a very significant contribution to the volatile matter collected. Moreover the differences in behavior between different coals of apparently similar rank may be due in part to differences in their content of sporinite and resinite. The inert macerals will decrease the yield, not merely because they are relatively inert diluents but also because they are likely to be efficient free radical traps in the early stages of the release of volatile matter.
Coking blends commonly contain the basic coal to provide the bulk of the coke matrix, a component designed to increase fluidity to the desired extent, and an inert diluent to increase the coke hardness. Clearly there are likely to be a range of three-component mixtures that will give the desired result. It is at least a theoretical possibility that one could select a mixture within the range such that inertinite is used as little as possible as an inert diluent and exinite-

containing material is used both to contribute fluidity and to increase the yield of by-products.

If still further departures from present practice can be considered, one might carbonize, perhaps in a fluidized bed, in the presence of additives. Additives could be gaseous and include steam and a little air, or be a solid and consist of a catalyst designed to assist the breakdown of volatile matter to simpler material immediately on release from the coal particles. In any case if one wishes to interfere with the carbonization mechanism in this or in any other way, one must obviously do it in the dissociation stage (380-480°) or earlier.

(c) Other Methods

At one time it was thought that coal might be like a polymer in containing a variety of monomer units linked together by a relatively weak bond, as in cellulose. This view can no longer be maintained; in so far as it is just to consider coal a type of polymer, the linking units are not weak but very strong. The hopes of finding a simple economically feasible means of breaking the structure down into useful chemicals as main rather than by-products are therefore small. The depolymerization of coal with the boron trifluoride/phenol complex, described by Heredy and Neuworth,[11] is a very interesting contribution to this problem and will no doubt be developed further.

The classical organic chemist's answer to the problem of breaking down a mixed aliphatic-aromatic structure is selective oxidation of the aliphatic parts. It has so far proved impossible to oxidize coal selectively in this sense, but in any case a range of aromatic acids will be the principal products; these may have practical applications, but necessarily only in a strictly limited field. The fluorination procedure described by Farendon and Pritchard[27] is another reaction that might give chemical products useful in a limited field.

Provided the bulk of the products could be sold at chemical rather than fuel prices, it might be possible to use exinite concentrates as raw materials for chemical processing, and they possess certain advantages. This is a possibility that should be explored further. The cannel and boghead coals are described as being largely exinite, but in view of their different origin it seems doubtful whether they are very similar to the exinite material associated with bituminous coals. However, they might be useful starting materials.

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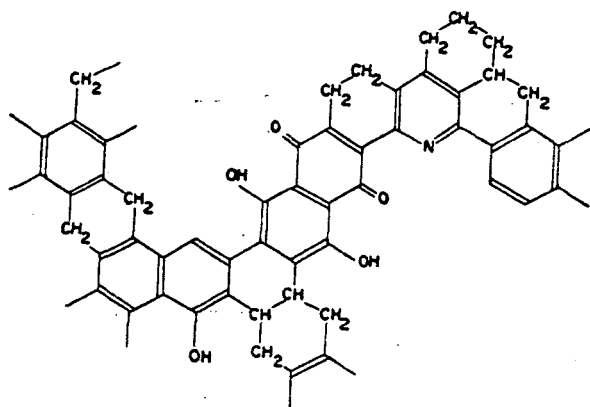
FIGURE 1. *Hypothetical segment of a typical molecule in a bituminous coal.*